ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM (EMSP) SYMPOSIUM

(Cosponsored with the Division of Analytical Chemistry)
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DIVISION OF ENVIRONMENTAL CHEMISTRY 225th American Chemical Society Meeting New Orleans, LA Wednesday, March 26, 2003

Organizer: T. Zachry

Presiding: T. Fryberger

Time	Paper
1:30 p.m.	Introductory Remarks.
1:35 p.m.	Use of sonication for in-well softening of semivolatile organic compounds. R.W. Peters, J.L. Manning and M.L. Wilkey
2:00 p.m.	Strategies for the engineered phytoremediation of mercury and arsenic pollution. R.B. Meagher and <u>O.P. Dhankher</u>
2:25 p.m.	A novel nuclear-cytoplasm shuttle protein in oxidative stress tolerance. <u>D.W. Ow</u> and W. Song
2:50 p.m.	Intermission.
3:15 p.m.	Genes that mediate arsenic and heavy metal detoxification in plants. D.A. Lee and <u>J.I. Schroeder</u>
3:40 p.m.	Molecular indicators of soil humification and interaction with heavy metals. T.WM. Fan, R.M. Higashi, T. Cassel, P. Green and A. Lane
4:05 p.m.	Peroxidase-catalyzed oxidative coupling of phenols in the presence of geosorbents. Q. Huang and W.J. Weber, Jr.
4:30 p.m.	Kinetic study of colloidal birnessite formation during oxidation of chlorinated solvent by permanganate. X.D. Li and F.W. Schwartz
4:55 p.m.	Concluding Remarks.

ABSTRACTS

Use of sonication for in-well softening of semivolatile organic compounds. Robert W. Peters¹, John L. Manning² and Michael L. Wilkey³; ¹Department of Civil and Environmental Engineering, University of Alabama at Birmingham, School of Engineering, 1075 13th Street South, Birmingham, AL 35294-4440, Fax: 205-934-9855, rpeters@eng.uab.edu; ²Vanderbilt University Medical Center, Vanderbilt University; ³TechSavants, Inc.

This study examined an integrated sonication/vapor stripping system's ability to remove/destroy chlorinated organics from groundwater. Chlorinated solvents studied included carbon tetrachloride, trichloroethylene, trichlorethane and tetrachloroethylene. Contaminant concentrations ranged from ~1 to ~100 mg/L. The sonicator had an ultrasonic frequency of 20 kHz; applied power intensities were 12.3-, 25.3- and 35.8-W/cm². Batch reactions were operated for up to 10 minutes treatment time, with samples drawn for GC analysis every 2 minutes. Batch experimental results were obtained using sonication, vapor stripping and combined sonication/vapor stripping. For the chlorinated solvents, the first order rate constants were in the range of 0.02 to 0.06 min¹, 0.23 to 0.53 min¹ and 0.34 to 0.90 min¹ for sonication, vapor stripping and combined sonication/vapor stripping. For the chlorinated organics (treatment time ~10 min.), the fraction remaining after sonication and vapor stripping ranged from 62% to 82%, while less than 3% remained from the combined sonication/vapor stripping system.

Strategies for the engineered phytoremediation of mercury and arsenic pollution. Richard B. Meagher and Om Parkash Dhankher; Department of Genetics, University of Georgia, Life Sciences Building, Room B402A, Athens, GA 30602, Fax: 706-542-1387, Meagher@arches.uga.edu, parkash@arches.uga.edu.

Phytoremediation is the use of plants to extract, transport, detoxify and/or sequester pollutants of the land, water or air. Mercury and arsenic are among the worst environmental pollutants, adversely affecting the health of hundreds of millions of people worldwide. We have demonstrated that plants can be engineered to take up and tolerate several times the levels of mercury and arsenic that would kill most plant species. Starting with methylmercury and/or ionic mercury contamination, mercury is detoxified, stored below or above ground, and even volatilized as part of the transpiration process and keeping it out of the food chain. Initial efforts with arsenate demonstrate that it can be taken up, transported aboveground, electrochemically reduced to arsenite in leaves and sequestered in thiol-rich peptide complexes. The transgenic mercury remediation strategies also worked in cultivated and wild plant species like canola, rice and cottonwood.

A novel nuclear-cytoplasm shuttle protein in oxidative stress tolerance. <u>David W. Ow</u> and Wen Song; Plant Gene Expression Center, USDA/UC Berkeley, 800 Buchanan St., Albany, CA 94710, Fax: 510-559-5678, ow@pgec.ars.usda.gov.

Plants for effective extraction of toxic metals and radionuclides must tolerate oxidative stress. To identify genes that enhance oxidative stress tolerance, an *S. pombe* cDNA expression plasmid library was screened for the ability to yield hypertolerant colonies. Here, we report on the properties of one gene that confers hypertolerance to cadmium and oxidizing chemicals. This gene appears to be conserved in other organisms as homologous genes are found in human, mouse, fruitfly and *Arabidopsis*. The fruitfly and *Arabidopsis* genes likewise enhance oxidative stress tolerance in fission yeast. During oxidative stress, the amount of mRNA does not change, but protein fusions to GFP relocate from the cytoplasm to the nucleus. The same pattern is observed with the *Arabidopsis* homologue-GFP fusion protein. This behavior suggests a signaling role in oxidative stress tolerance and these conserved proteins may be targets for engineering stress tolerant plants for phytoremediation.

Genes that mediate arsenic and heavy metal detoxification in plants. David A. Lee and <u>Julian I. Schroeder</u>; Division of Biology, University of California, 9500 Gilman Dr., La Jolla, CA 92093-0346, dlee@biomail.ucsd.edu, jischroeder@ucsd.edu.

To gain insight into the mechanisms of arsenic tolerance in plants, we developed a genetic screen to isolate *Arabidopsis thaliana* mutants with altered tolerance to arsenic. We report here on the isolation of *ars1*, a novel mutant with significantly increased tolerance to arsenate. *ars1* accumulates similar levels of arsenic as wild type plants, but *ars1* tolerance does not appear to be phytochelatin or glutathione dependent. *ars1* plants do have a higher rate of phosphate uptake than wild type plants and plants grown with an excess of phosphate show increased tolerance to arsenate. Traditional models of arsenate tolerance in plants are based on the suppression of phosphate uptake pathways and, consequently, the reduced uptake of arsenate. Our data suggest that arsenate tolerance in *ars1* is due to a new mechanism mediated by increased phosphate uptake in *ars1*. Results exploring increased metal tolerance through engineered phytochelatin expression will also be discussed.

Molecular indicators of soil humification and interaction with heavy metals. <u>Teresa W.-M. Fan</u>¹, Richard M. Higashi², Teresa Cassel², Peter Green² and Andrew Lane¹; ¹Department of Chemistry, University of Louisville, 2320 S. Brook St., Louisville, KY 40292, Fax: 502-852-8149, twfan@earthlink.net; ²Crocker Nuclear Laboratory, Univ. of California-Davis.

For stabilization of heavy metals at contaminated sites, interaction of soil organic matter (SOM) with heavy metal ions is critically important for long-term sustainability, a factor that is poorly understood at the molecular level. Using ¹³C- and ¹⁵N-labeled soil humates (HS), we investigated the turnover of five organic amendments (celluose, wheat straw,

pine shavings, chitin and bone meal) in relation to heavy metal ion leaching in soil column experiments. The labeled molecular substructures in HS were examined by multinuclear 2-D NMR and pyrolysis GC-MS while the element profile in the leachates was analyzed by ICP-MS. Preliminary analysis revealed that peptidic and polysaccharidic structures were highly enriched, which suggests their microbial origin. Cd(II) leaching was significantly attenuated with humification of lignocellulosic materials. Correlation of ¹³C and ¹⁵N turnovers of HS substructures to metal leaching is underway.

Peroxidase-catalyzed oxidative coupling of phenols in the presence of geosorbents. Qingguo Huang¹ and Walter J. Weber, Jr.²; ¹Environmental and Water Resources Engineering, Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor, MI 48109-2125, qingguoh@umich.edu; ²Department of Civil and Environmental Engineering, University of Michigan.

This study focuses on elucidation of the reaction behaviors of peroxidase-mediated phenol coupling in the presence of soil/sediment materials. Our goal is a mechanistic understanding of the influences of geosorbent materials on enzymatic coupling reactions in general and the development of methods for predicting such influences. Extensive experimental investigations of coupling reactions were performed under strategically selected conditions in systems containing model geosorbents having different properties and chemical characteristics. The geosorbents tested were found to influence peroxidase-mediated phenol coupling through one or both of two principal mechanisms; *i.e.*, i) mitigation of enzyme inactivation and/or ii) participation in cross-coupling reactions. Such influences were found to correlate with the chemical characteristics of the sorbent materials and to be simulated well by a modeling approach designed in this paper. The results of the study have important implications for potential engineering implementation and enhancement of enzymatic coupling reactions in soil/subsurface remediation practice.

Kinetic study of colloidal birnessite formation during oxidation of chlorinated solvent by permanganate. X. David Li and Franklin W. Schwartz; Department of Geological Sciences, The Ohio State University, 223 Mendenhall Lab, 125 S. Oval Mall, Columbus, OH 43210, Fax: 614-292-7688, li@geology.ohio-state.edu.

The use of permanganate for the *in situ* oxidation of chlorinated ethylenes has shown promise in the remediation of subsurface contamination. The oxidation reaction produces Mn oxide, which causes pore plugging and problems in oxidant delivery. This study utilized batch experiments to explore the feasibility of using phosphate to slow down the formation of colloidal Mn oxide, which may allow Mn oxide to precipitate further away from the zone of oxidation. The results show that phosphate can influence the formation of the colloids. Colloid growth was slow, especially early in the reaction. The rate of the colloid formation decreases linearly with increasing concentrations of phosphate ion. Efforts were made to elucidate the mechanism of the reaction between phosphate and Mn oxide. A model was proposed to describe the reaction process,

which is thought to involve the formation of a Mn(IV)-phosphate complex in the aqueous phase before formation of the colloids.	3